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Reduction Studies of NiO Powder using Hydrogen

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Beamline(s): X7B

Introduction: Reduction of metal oxides using hydrogen is a frequently used method to prepare active catalysts and electronic devices. Studies of the reaction of hydrogen on a metal oxide surface will provide fundamental information about the reduction process in industrial applications.

Methods and Materials: Commercially obtained NiO powders (>99.99% purity) were loaded in an open sapphire capillary which has an inner diameter of 0.2 mm flowing 5% H₂/95% He gas mixture (flow rate \approx 5~15 cc/min). A heater was designed by winding a kanthal wire around the capillary which also contains the sample (see the figure 1). Prior to experiments, temperature of the sample was calibrated by measuring a coefficient of thermal expansion from Y₂O₃ powder. Diffraction data were recorded isothermally at temperatures in the range of 250°C ~320°C under flowing 5% hydrogen gas mixture using a MAR345 area detector.

Results: Figure 2 is a plot for the time-resolved x-ray diffraction data illustrating decay the NiO phase (fcc, $a=4.17\text{\AA}$) under hydrogen environment at constant temperature (280°C). During the first 50 minutes, no major changes are observed in NiO peaks. After an induction period, however, metallic Ni phase peaks (fcc, $a=3.52\text{\AA}$) start appear when NiO peaks decay. There is no hint of an intermediate phase during the process. Figure 3 shows the decay of the NiO (220) peaks produced by reaction with hydrogen as a function of time at different isothermal conditions. With increasing temperature this clearly shows i) the decreased induction period and ii) the increased reduction rate. This trend has also been observed in photoemission (U7A beamline) and EXAFS (X16C beamline) experiments. Density functional calculations have shown that hydrogen binds and reacts with O defects much better than with “smooth” NiO surface. The trend in the induction time can be rationalized with this model which suggest that the defects are more difficult to develop at the beginning, but will form more readily at higher temperatures [1].

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References: [1] J.A. Rodriguez, J.C. Hanson, A.I. Frenkel, J.Y. Kim, and M. Perez. *J. Am. Chem. Soc.* (in press).

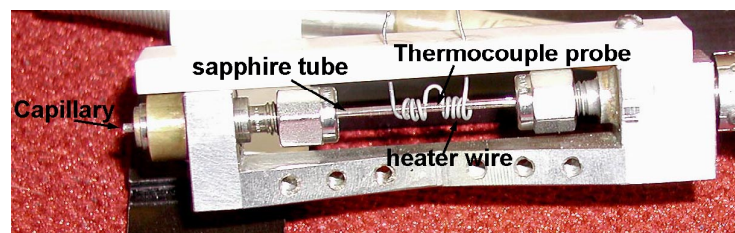


Figure 1. A heater designed for powder diffraction using capillary samples.

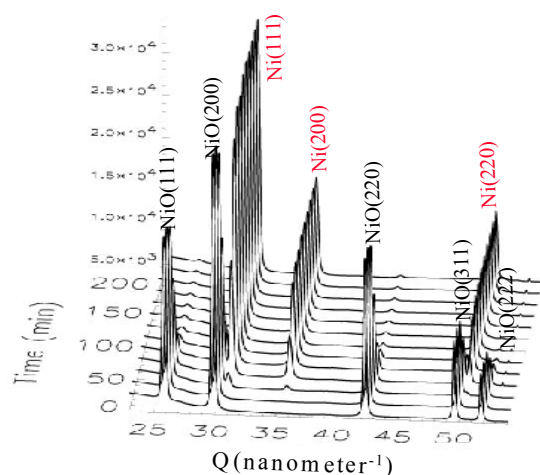


Figure 2. Time resolved x-ray diffraction data for the isothermal reduction of NiO powder at 280°C under 5% H₂ gas mixture.

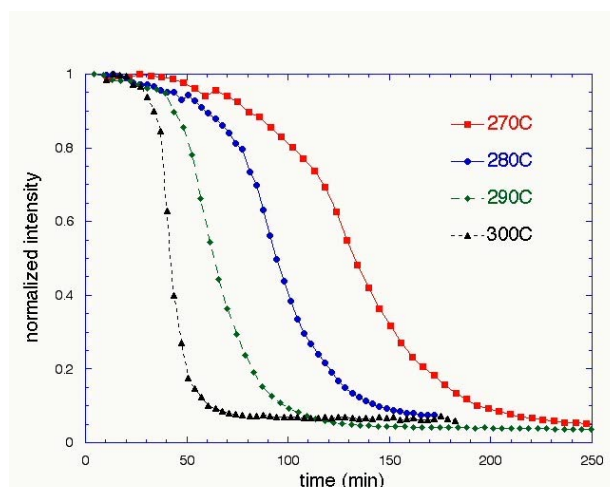


Figure 3. Peak intensities of NiO (111) phase as a function of time during isothermal reductions at 270, 280, 290, and 300°C.